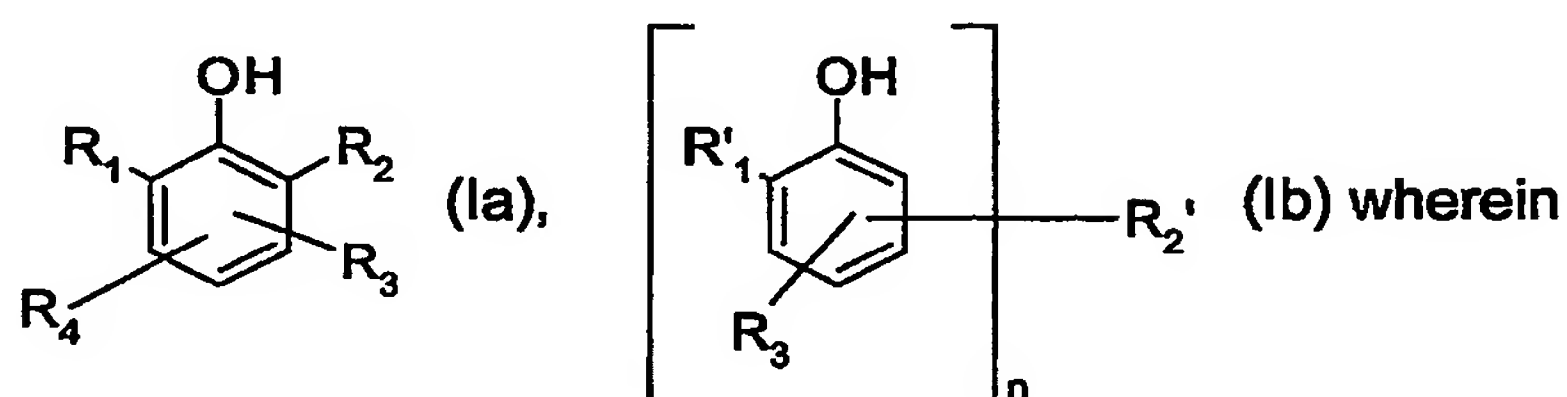


Claims

1. A composition comprising

- c) a halogen containing polymer or copolymer in the form of an aqueous suspension or emulsion;
- d) a sterically hindered phenolic antioxidant with a melting point of more than 20° C containing a compound of formula (Ia) or (Ib)



n is 2 or 3

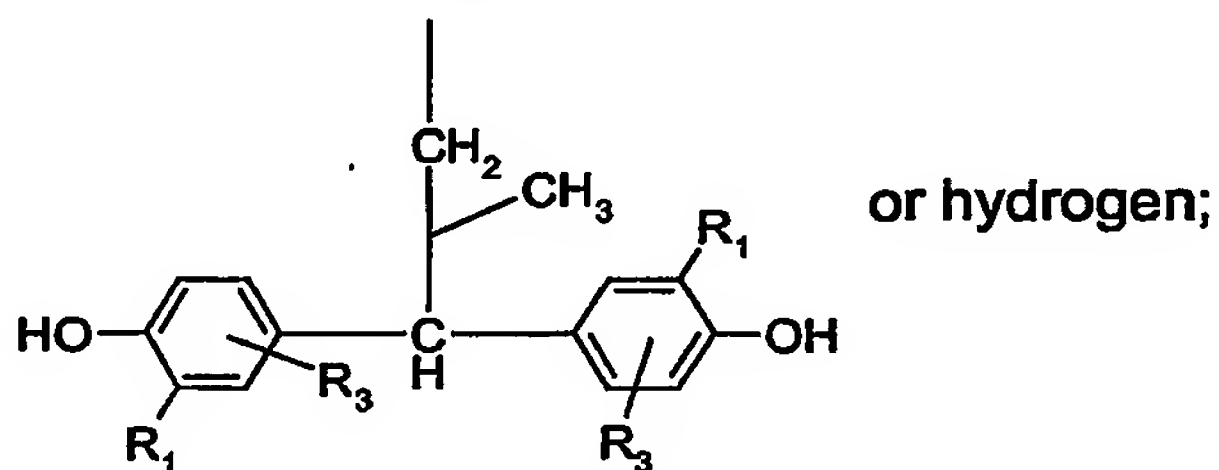
R₁ is tert.-butyl, secondary bound C₃-C₁₈alkyl or C₅-C₆cycloalkyl;

R'₁ is tert. butyl, primary or secondary bound C₁-C₁₈alkyl, phenyl, C₇-C₉phenyl-alkyl or C₅-C₆cycloalkyl;

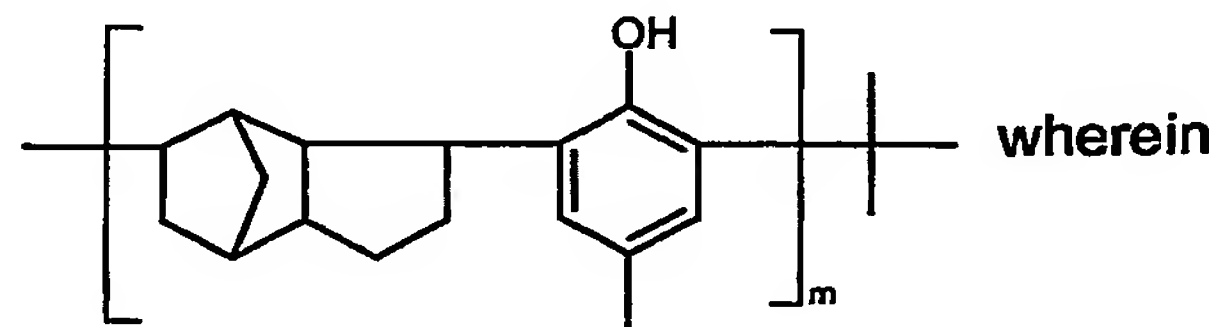
R₃ is C₁-C₁₈ alkyl, C₁-C₁₈alkoxy, C₅-C₆cycloalkyl or -CH₂-CH₂-CO-O-(C₁-C₁₈)alkyl;

R'₂ is a divalent or trivalent bridging group;

R₄ is a group



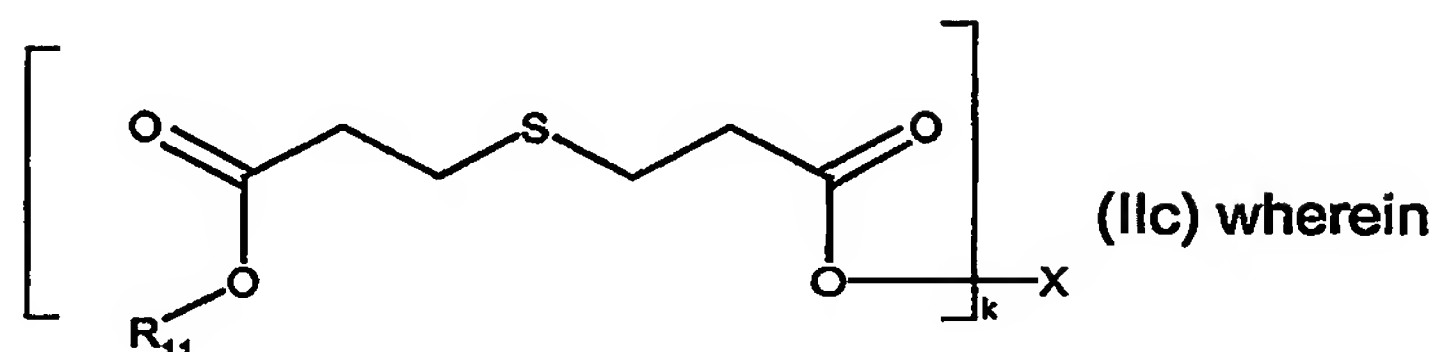
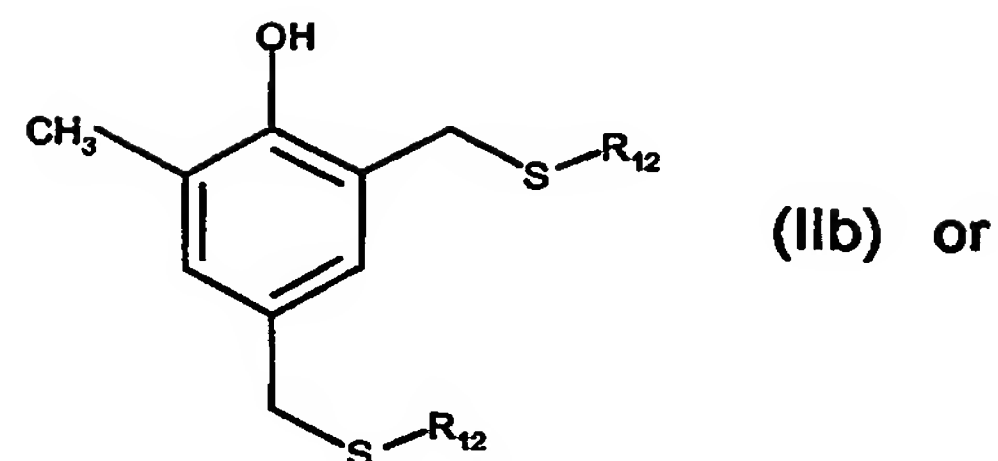
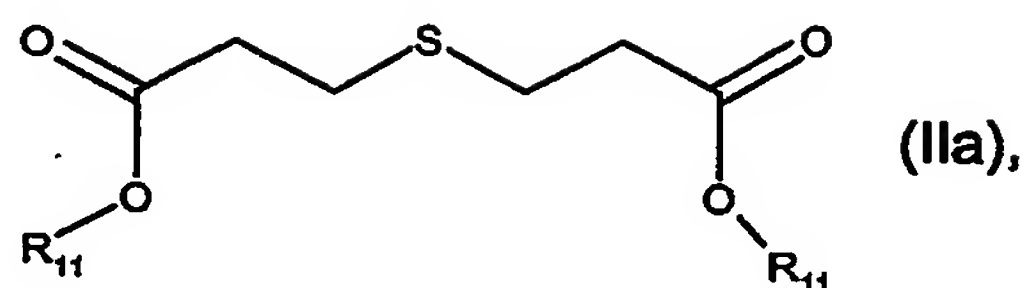
R₂ is hydrogen, methyl or a group



m is a number from 1 to 10; and

- c) a thioether or thioether-ester with a melting point of more than 20° C of formula (IIa), (IIb) or (IIc)

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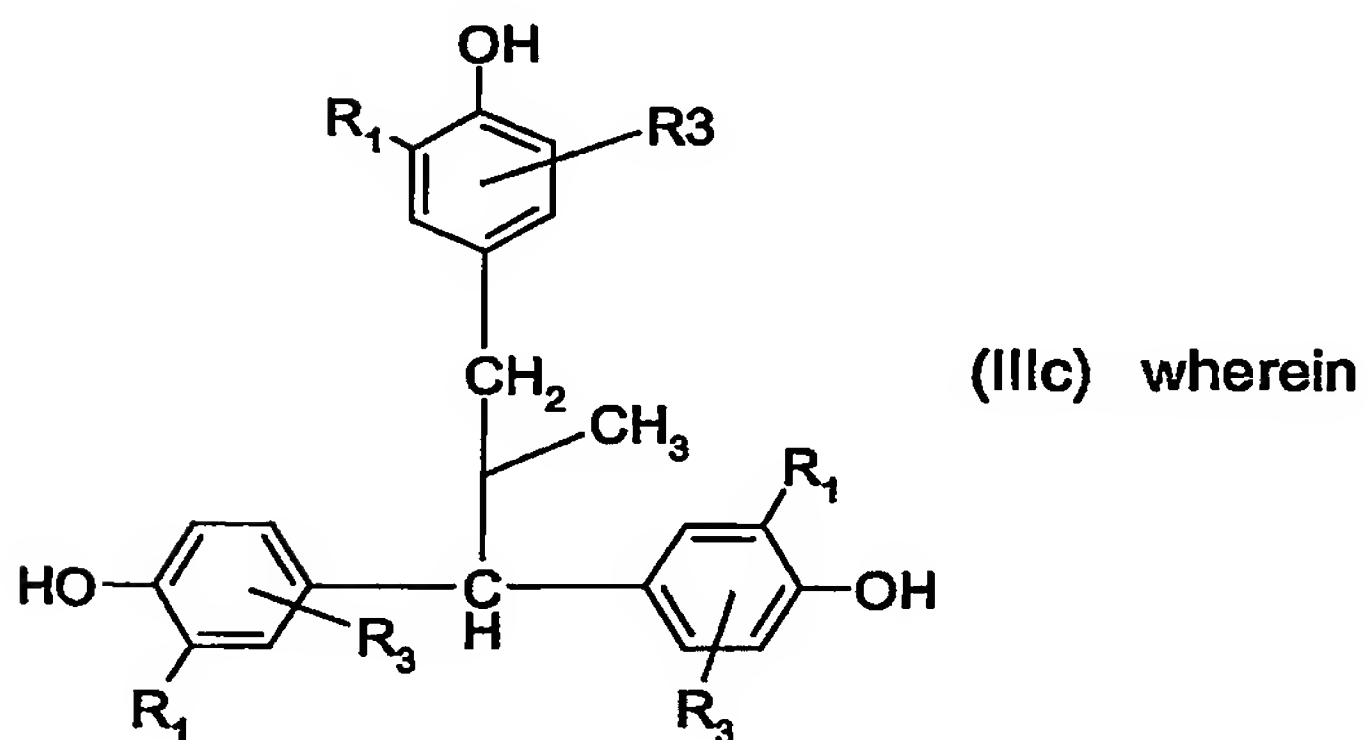
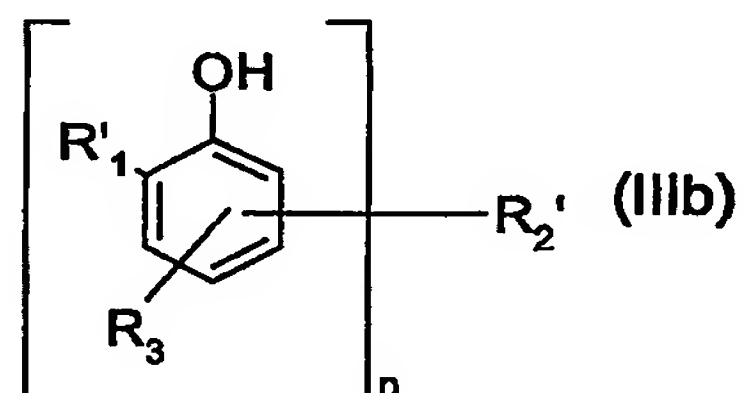
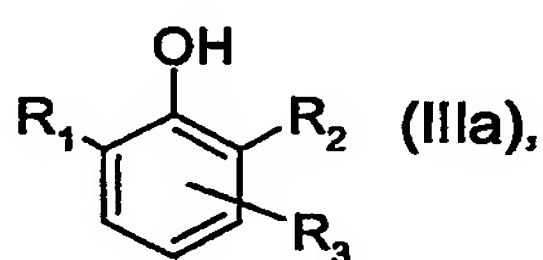


R_{11} and R_{12} are independently C_1 - C_{18} alkyl

k is 2-4; and

X is 2-methyl-1,2,3-propane-triyl- or 1,2,3,4-methane-teteryl-.

2. A composition according to claim 1 wherein the sterically hindered phenolic antioxidant containing a structural element of formula (Ia) or (Ib) is of formulae (IIIa), (IIIb) or (IIIc)



n is 2 or 3

R_1 is tert.-butyl, secondary bound C_3 - C_{18} alkyl or C_5 - C_6 cycloalkyl;

R'_1 is tert. butyl, primary or secondary bound C_1 - C_{18} alkyl, phenyl, C_7 - C_9 phenyl-alkyl or C_5 - C_6 cycloalkyl;

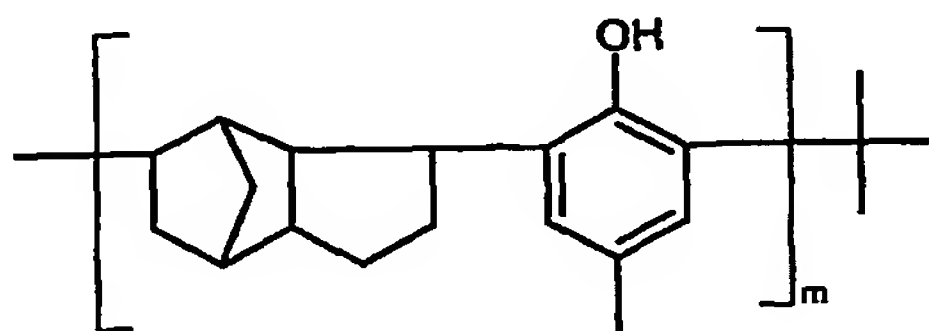
R_3 is C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, C_5 - C_6 cycloalkyl or a group

$-\text{CH}_2\text{-CH}_2\text{-CO-O-(C}_1\text{-C}_{18}\text{)alkyl}$;

R'_2 is C_1 - C_{12} alkylene, $-\text{S}-$, trimethylene-isocyanurate, or a group

$-\text{CH}_2\text{-CH}_2\text{-CO-(OCH}_2\text{CH}_2\text{)}_p\text{-O-CO-CH}_2\text{CH}_2\text{-}$ wherein p is a number from 1 to 3;

5 R_2 is hydrogen, methyl or a group



wherein m is a

number from 1 to 10.

3. A composition according to claim 1 wherein the halogen containing polymer is PVC.

10 4. A composition according to claim 1 wherein in component c) both R_{11} are C_{12} alkyl or C_{18} alkyl and the R_{12} are C_{12} alkyl.

5. A composition according to claim 1 wherein in component b) the sterically hindered phenolic antioxidant is

15 2-tert-butyl-4,6-dimethylphenol;

2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltetradec-1'-yl)phenol and mixtures thereof;

2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol),

20 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol)

or

(ethylenebis(oxyethylene)bis[3-(5-tert-butyl-4-hydroxy-m-tolyl)propionate].

25 6. A composition according to claim 1 wherein in component b) the sterically hindered phenolic antioxidant is

2-tert-butyl-4,6-dimethylphenol, 2,4-dimethyl-6-(1'-methyltetradec-1'-yl)phenol or a mixture thereof

and component c) is

30 di-lauryl-thio-di-propionate, di-stearyl-thio-di-propionate or a mixture thereof.

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7. A composition according to claim 1 wherein in component b) the sterically hindered phenolic antioxidant is

2,4-dimethyl-6-(1'-methyltetradec-1'-yl)phenol

and component c) is

5 di-lauryl-thio-di-propionate.

8. A composition according to claim 1 wherein the sterically hindered phenolic antioxidant, component b) is present in an amount from 50 ppm to 2000 ppm based on the weight of the halogen containing monomer.

10

9. A composition according to claim 1 wherein component c) is present in an amount from 50 ppm to 2000 ppm based on the weight of the halogen containing monomer.

10. A composition according to claim 1 wherein the ratio of component b) to component c) is from 1:10 to 10:1.

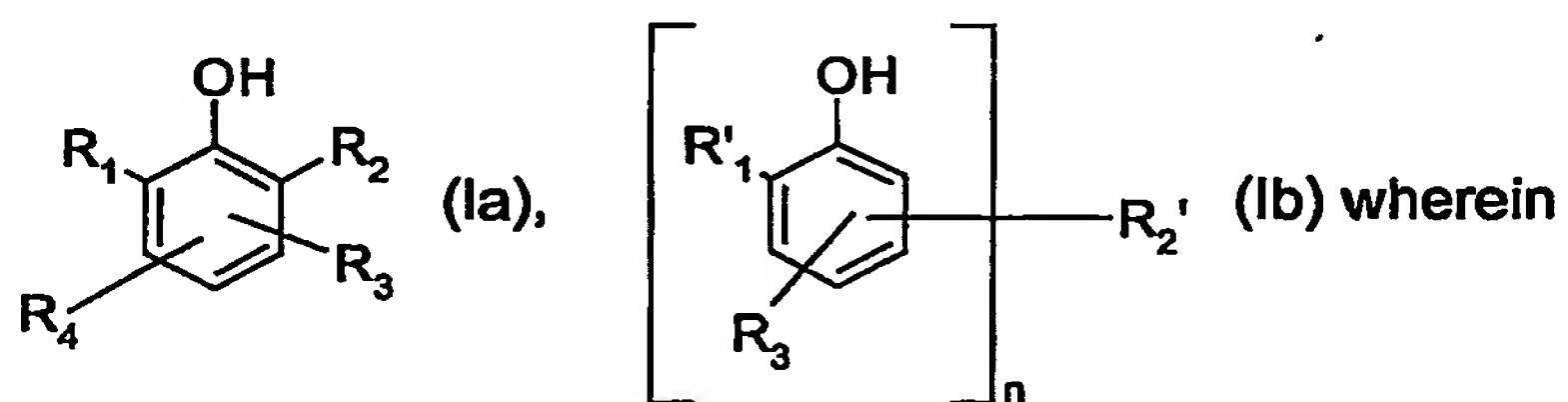
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11. A composition according to claim 1, which additionally contains a sterically hindered phenolic antioxidant different from that of component b), a phosphorous containing stabilizer, a 2-benzofuranone stabilizer, a sterically hindered amine light stabilizer or a UV-absorber.

20

12. A process for the stabilization of halogen containing polymers against thermal degradation, which process comprises adding to the halogen containing polymer, which is in an aqueous suspension or emulsion during or after the polymerization process

25 b) a sterically hindered phenolic antioxidant with a melting point of more than 20° C containing a compound of formula (Ia) or (Ib)



n is 2 or 3

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R₁ is tert.-butyl, secondary bound C₃-C₁₈alkyl or C₅-C₆cycloalkyl;

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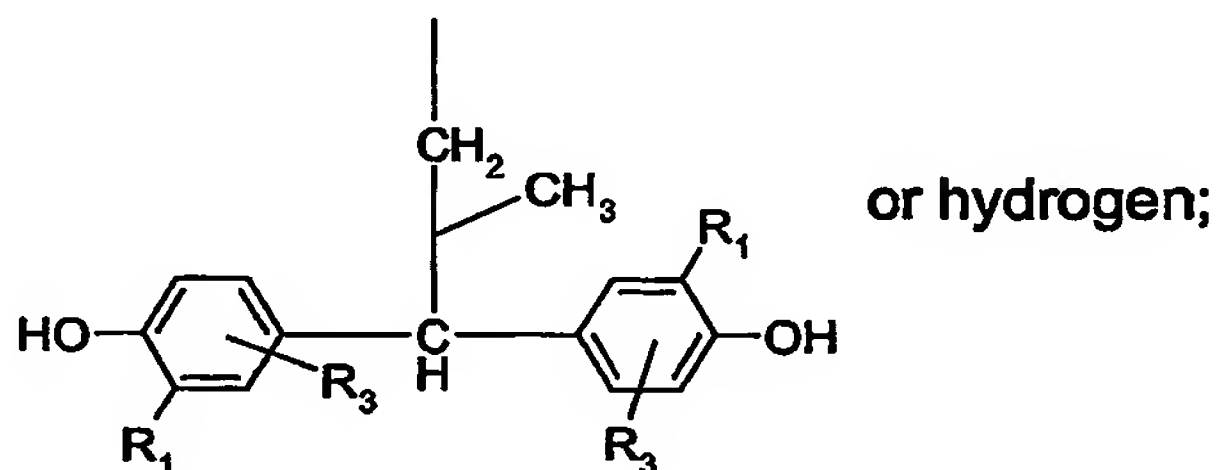
R'_1 is tert. butyl, primary or secondary bound C_1 - C_{18} alkyl, phenyl, C_7 - C_9 phenyl-alkyl or C_5 - C_6 cycloalkyl;

R_3 is C_1 - C_{18} alkyl, C_1 - C_{18} alkoxy, C_5 - C_6 cycloalkyl or $-\text{CH}_2\text{-CH}_2\text{-CO-O-(C}_1\text{-C}_{18}\text{)alkyl}$;

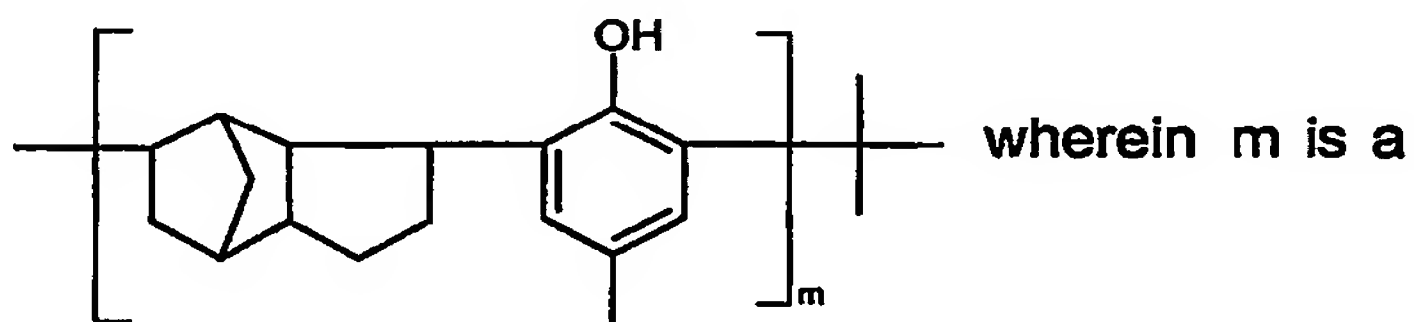
R'_2 is a divalent or trivalent bridging group;

5

R_4 is a group



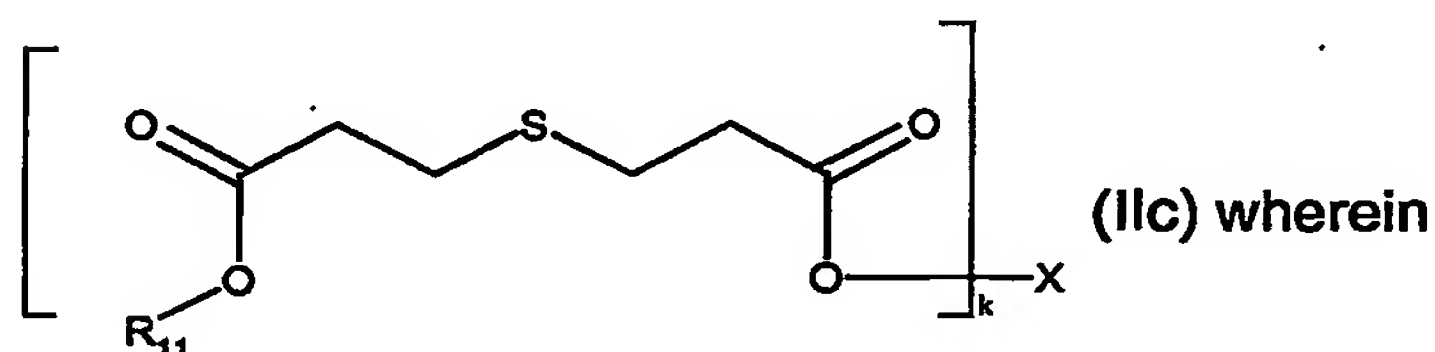
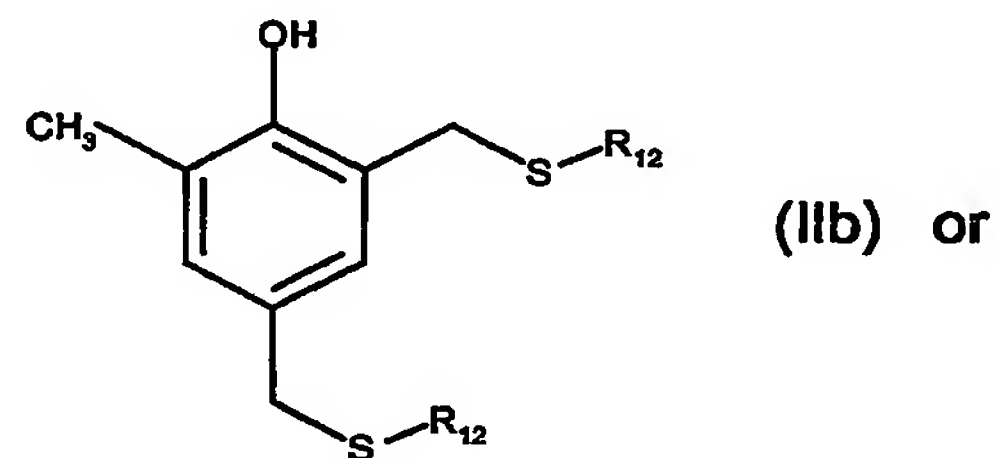
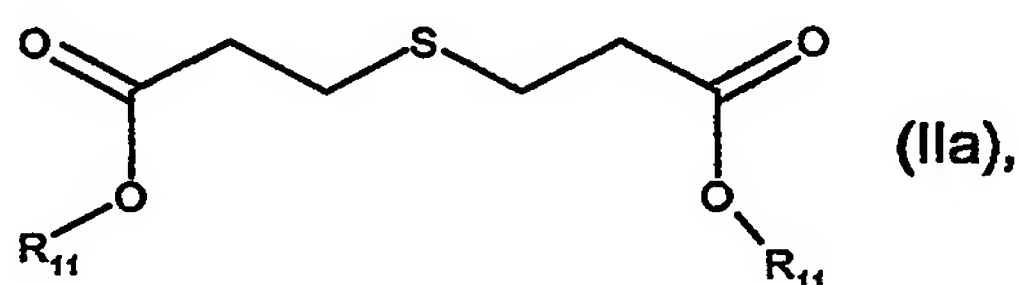
R_2 is hydrogen, methyl or a group



number from 1 to 10; and

c) a thioether or thioether-ester with a melting point of more than 20°C of formula (IIa), (IIb) or (IIc)

10



R_{11} and R_{12} are independently C_1 - C_{18} alkyl

k is 2-4; and

X is 2-methyl-1,2,3-propane-triyl- or 1,2,3,4-methane-tetryl-.

15

13. A process according to claim 12 wherein the components b) and c) are added towards the end of the polymerization reaction.

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14. A process according to claim 12 wherein the polymerization is a suspension polymerization and the components a) and b) are added as an emulsion to the slurry towards the end of the polymerization reaction.

- 5 15. Use of a sterically hindered phenolic antioxidant with a melting point of more than 20° C together with a thioether or thioether-ester with a melting point of more than 20° C according to claim 1 for the thermal stabilization of aqueous suspensions or emulsions of halogen containing polymers.